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BY

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A DEPARTMENT OF COMMERCE - BUREAU OF MINES

A REVISION OF THE FREE ENERGY OF FORMATION OF SULPHUR DIOXIDE[1]

By E. D. Eastman[2]

The recent determination by Eckman and Rossini[3] of the heat of formation of sulphur dioxide appears to be of much greater accuracy than any previous measurement. The value obtained by them, 70,940 cal., is in good agreement with that of Thomsen (71,080), but differs by about 1,700 calories from Berthelot's result (69,260), and by 1,940 calories from the provisional figure (69,000) adopted by Lewis and Randall[4] in their studies of the free energies of the sulphur compounds. This large discrepancy suggested the desirability of a recalculation of the free energy of sulphur dioxide. In addition it is now possiblt to fix the specific heat of S_2 gas with greater certainty than at the time of the original calculations. These two changes are incorporated in the recalculations described below, and directly affect the values of ΔH_0 and the $\Delta\Gamma$ terms in the free energy equation. In the determination of the integration constant of the latter equation, the free energies and specific heats of water vapor and the oxides of carbon are required as auxiliary data. In this work these are based, with certain exceptions, upon the equations previously deduced,[5],[6] which differ appreciably from the corresponding equations of Lewis and Randall.

The principal equilibria employed below, and the plan of calculation, remain the same as in the calculations of Lewis and Randall. Before beginning this revision a search of the literature was made, extending to August, 1930, for studies of additional equilibria. Only one reaction was found that gives promise of increased accuracy. This is the equilibrium of sulphur dioxide with copper, cuprous oxide, and cuprous sulphide. In this case, however, certain of the subsidiary data are lacking, and until they become available, the existing studies of the equilibrium in this system can not be successfully utilized. The changes in the numerical data mentioned above, especially in the thermochemical constants, are therefore solely responsible for the rather significant differences of the revised from the original values of the free energy.

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1 The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6454."

2 Consulting physical chemist, Metallurgical Division, U. S. Bureau of Mines.

3 Eckman, J. R., and Rossini, Frederick D., The Heat of Formation of Sulphur Dioxide: Bureau of Standards Jour. of Research, vol. 3, 1929, pp. 597-618.

4 Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances: McGraw Hill Book Co., New York, 1923, 1st ed., 653 pp.

5 Eastman, E. D., The Free Energy of Water, Carbon Monoxide, and Carbon Dioxide: Inf. Cir. 6125, Bureau of Mines, May, 1929, 15 pp.

6 Eastman, E. D., Specific Heats of Gases at High Temperatures: Tech. Paper 445, Bureau of Mines, 1929 27 pp.

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FORMULATION OF THE FREE ENERGY EQUATION

Specific Heat Data

The specific heats required in these calculations have been expressed by the following equations:

$$S\ (rhomb.);\quad C_p = 4.12 + 4.7 \times 10^{-3}\ T$$
$$S_2(g);\quad C_p = 8.30 + 0.3 \times 10^{-3}\ T$$
$$O_2;\quad C_p = 6.76 + 0.606 \times 10^{-3}\ T + 0.13 \times 10^{-6}\ T^2$$
$$SO_2(g);\quad C_p = 7.70 + 5.30 \times 10^{-3}\ T - 0.83 \times 10^{-6}\ T^2$$

The equation for rhombic sulphur is that given by Lewis and Randall. For oxygen and sulphur dioxide the equations are those previously derived.[7] It will be recalled that for lack of detailed data sulphur dioxide was assumed to be identical with carbon dioxide in its specific heat. This is probably not as nearly correct as might be desired, and when more accurate equilibrium data are obtained this equation should be reconsidered. The only case requiring extended comment here, however, is that of S_2 gas, which will now be discussed.

Lewis and Randall took the heat capacity of S_2 the same as that of O_2. In the previous paper on specific heats,[8] however, it was pointed out that many of the more loosely bound diatomic molecules take up appreciable quantities of vibrational energy at relatively low temperatures. It was pointed out there that S_2 was more nearly like Cl_2 in this regard than any of the other gases, and might be roughly classed with it. A more exact consideration of the course of its specific heat curbe shows appreciable differences from the chlorine equation and seems to require separate treatment.

When the characteristic frequency of vibration of a diatomic molecule in the lowest state is known, it is possible to represent its vibrational specific heat approximately by means of the corresponding "Einstein function." In the case of S_2 the first quantum jump in vibration is approximately known, at least, from the calculation of Birge[9] based on spectral data. Taking this jump as 0.089 volt-equivalent, the corresponding Einstein function gives the values in Table 1 for vibrational heat capacity. The total heat capacities given there are then obtained by adding these values to 7/2 R, the molal heat capacity at constant pressure of a diatomic gas with rotational degrees of freedom fully excited.

Table 1.- Calculated heat capacity at constant pressure in calories per mol. of S_2 gas

T	C vibrational	C_p total	C_p equation	C_p L. & R.
250	0.56	7.52	8.38	6.75
300	0.80	7.76	8.39	6.80
500	1.41	8.37	8.45	7.00
750	1.70	8.66	8.53	7.25
1,000	1.82	8.78	8.60	7.50
1,500	1.90	8.86	8.75	8.00
2,000	1.94	8.90	8.90	8.50
2,500	1.96	8.92	9.05	9.00

7 Eastman, E. D., Specific Heats of Gases at High Temperatures: Tech. Paper 445, Bureau of Mines, 1929, 27 pp.

8 See footnote 7.

9 Birge, Raymond T., International Critical Tables: vol. 5, McGraw-Hill Co., New York, 1929.

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As will be seen from the table, the heat capacity of S_2 is rapidly varying in the temperature range immediately above 300°K. The form of this variation, moreover, is not representable over wide temperature intervals by simple equations of the usual algebraic type. One must therefore choose, if this type of equation is retained, between some sacrifices of accuracy or an extremely cumbersome equation. In this case the first course has been followed, since only moderate accuracy may be claimed in other portions of the work. The equation given above results in values of heat capacity shown in Table 1 under the heading C_p equation. At 300°K. the value from the equation differs by 8.1 per cent from the value assumed to be correct. At 500° this difference is reduced to 1 per cent; and in the interval 600 to 2,000° it never exceeds 2 per cent. This equation also should be revised when more accurate equlibrium data are available, but is believed adequate for the present purpose. For comparison, values calculated from the equation used by Lewis and Randall are shown in the last column of the table.

Heats of Reaction

The reactions in which we are interested are

$$1/2\ S_2(g) + O_2 = SO_2\ (g) \qquad \text{I}$$

and

$$S\ (\text{rhomb.}) + O_2 = SO_2\ (g) \qquad \text{II}$$

The value of ΔH in reaction II, ($\Delta H(II)$), was directly determined at 298°K. by Eckman and Rossini as -70,940 cal. To obtain $\Delta H(I)$ at 298°, Lewis and Randall resorted to an indirect determination through a value calculated from free energy changes in the reaction

$$2\ S(\text{rhomb.}) = S_2\ (g) \qquad \text{III}$$

Using the specific heat equations given above, we have

$$\Delta C_p(III) = 0.06 - 9.1 \times 10^{-3}T$$

$$\Delta H(III) = \Delta H_0(III) + 0.06\ T - 4.55 \times 10^{-3}T^2$$

and

$$\Delta F°(III) = \Delta H_0(III) - 0.06\ T\ \ln T + 4.55 \times 10^{-3}T^2 + I_1T \qquad (1)$$

From the values of $\Delta F°(III)$ obtained by Lewis and Randall at 718° and 298°K., namely 3,320 cal. and 18,280 cal., both $\Delta H_0(III)$ and I_1 may be calculated. The resulting values are $\Delta H_0 = 29{,}840$ cal. and $I_1 = -39.81$. Lewis and Randall, taking the heat capacity of S_2 the same as of O_2, found $\Delta H_0 = 30{,}580$ cal., and $I_1 = -52.4$. $\Delta H_{298}(III)$ is calculated from the above values to be 29,454 cal., as compared with 29,690 cal. found by Lewis and Randall.

Combining $\Delta H(II)$ and $\Delta H(III)$ as found above gives $\Delta H_{298}(I) = -85{,}667$ cal. From the equation

$$\Delta C_p(I) = -3.21 + 4.544 \times 10^{-3}T - 0.96 \times 10^{-6}T^2,$$

it is seen that

$$\Delta H(I) = \Delta H_0(I) - 3.21\ T + 2.272 \times 10^{-3}T^2 - 0.32 \times 10^{-6}T^3.$$

Employing $\Delta H_{298}(I)$ found above, $\Delta H_0(I)$ becomes -84,905 cal.

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The Free Energy Equation

The various data obtained above may be combined to give the free energy equation for reaction I, i.e., for the formation of SO_2 gas from S_2 gas and oxygen. It is

$$\Delta F°(I) = -84905 + 3.21\ T\ \ln T - 2.272 \times 10^{-3}T^2 + 0.16 \times 10^{-6}T^3 + I_2T \quad (2)$$

The integration constant, I_2, of this equation is then to be determined from the equilibria discussed below.

DETERMINATION OF THE INTEGRATION CONSTANT

The first equilibrium employed by Lewis and Randall for the determination of I_2 is that between water vapor, liquid sulphur, hydrogen sulphide, and sulphur dioxide at the boiling point of sulphur. From their studies of this equilibrium they obtained the free energy change at this temperature in the reaction

$$2H_2O(g) + 3/2\ S_2(g) = 2H_2S(g) + SO_2(g). \qquad IV$$

Their value is $\Delta F°_{718}(IV) = 2,250$ cal. Calculating from their equation XXXVIII, - 22 the free energy of $H_2S(g)$ at 718°, one finds -12,860 cal. The free energy of water vapor, from the equation previously referred to[10], is -49,293 cal. at 718°. These values combined give the free energy of SO_2 at 718° as -70,614 cal. The latter value substituted in equation (2), leads to the value $I_2 = 0.34$.

The second calculation of I_2 is based upon the equilibrium studies of Randall and Bichowsky. From their work Lewis and Randall have derived values of the equilibrium constants, K(V) in the reaction

$$3H_2 + SO_2 = H_2S + 2H_2O. \qquad V$$

Combining the equations already referred to of Lewis and Randall for the free energy of H_2S, and that of Eastman for H_2O, leads to an expression for I_2 as follows:

$$I_2 = R\ \ln K(V) - 48750/T + 1.75\ \ln T + 4.355 \times 10^{-3}T - 0.882 \times 10^{-6}T^2 - 2.83$$

With the values of log K(V) from Table 3 of Lewis and Randall[11] the following values of I_2 are found:

T	1160	1362	1473	1473	1645
I_2	-1.49	-1.87	-2.29	-2.62	-3.15

The third calculation utilizes the data obtained by Ferguson in his study of the reduction of SO_2 by CO. Lewis and Randall write the reaction

$$2CO_2 + 1/2\ S_2 = 2CO + SO_2 \qquad VI$$

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10 Eastman, E. D., The Free Energy of Water, Carbon Monoxide, and Carbon Dioxide: Inf. Cir. 6125, Bureau of Mines, May, 1929, 15 pp.

11 Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances: McGraw Hill Book Co., New York, 1923, p. 546.

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and summarize Ferguson's data by means of two values of log K(VI), namely, -3.56 at 1,275°K. and -2.38 at 1,460°K. The equation for the calculation of I_2, obtained by combination of equation 2 with the equations for the free energies of CO and CO_2, is

$$I_2 = -R \ln K(VI) - 49150/T + 6.93 \ln T - 13.118 \times 10^{-3}T + 4.204 \times 10^{-6}T^2 - 6.516 \times 10^{-10}T^3 - 15.68$$

From the values above of log K(VI), I_2 is found to be 0.37 and -0.22 at the two temperatures given.

The data respecting I_2 from the three sources above is summarized in Table 2.

Table 2.- Comparison of values of the integration constant, I_2, of the free energy equation

Reaction	Average I_2	Deviation	Trend
Sulphur and water at 718°K.	0.34	0.6	-
Sulphur and water, 1,160 to 1,645°K.	-2.28	.3	1.7
Reduction of SO_2 by CO, 1,275 and 1,460°K.	0.15	0.6	0.6

The "deviations" in Table 2 are estimates of the approximate deviation of results at a single temperature from their mean, while the "trend" shows the extreme variation of values at different temperatures.

The agreement between the first and third values of I_2 in Table 2 is about the same as in the calculations of Lewis and Randall, while the second is a little further removed from the other two. The trends in I_2 in the last two series are also slightly increased. The remark of Lewis and Randall that, considering the difficult nature of the equilibrium measurements the agreement is surprisingly good, still applies. This is especially true in view of some obvious uncertainties that still remain in the subsidiary data. One of the more important of these is in the heat of formation and specific heat of H_2S, the free energy of which enters in several places in these calculations. The heat of formation was calculated by Lewis and Randall from equilibrium measurements at high temperatures. The specific heats of S_2 gas and H_2S used by them in their calculations are both too low. These errors are at least partly compensating, and judging from such tests of the results as may be applied, may be very closely compensated. This has been assumed to be the case in the present calculation, no attempt being made to improve the ΔC_p values for this substance. For more accurate work this should, however, be considered, as should also those for SO_2.

Of the three sets of measurements above, the first represents the smaller extrapolation from the standard temperature, while the third is perhaps more direct and less affected by multiple errors than the others; both seem preferable to the second series. The value of I_2 in equation (2) is therefore chosen as 0.25, giving some weight to both the first and third methods, but excluding the second.

This value of I_2 used in equation (2) gives $\Delta F° = -79,580$ at 298°K. as the free energy of formation of SO_2 from S_2 gas. Combined with equation (1), its free energy from rhombic sulphur is found to be -70,440 cal

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SUMMARY OF RESULTS

The recalculations described above lead to the following revised equations:

$2\ S(\text{rhomb.}) = S_2(g)$; $\Delta F^\circ_{298} = 18{,}280$

$\Delta F^\circ = 29{,}840 - 0.06\ T \ln T + 4.55 \times 10^{-3} T^2 - 39.81\ T$

$1/2\ S_2(g) + O_2 = SO_2(g)$; $\Delta F^\circ_{298} = -79{,}580$ cal.

$\Delta F^\circ = -84{,}905 + 3.21\ T \ln T - 2.272 \times 10^{-3} T^2 + 0.16 \times 10^{-6} T^3 + 0.25\ T$

$S(\text{rhomb.}) + O_2 = SO_2(g)$; $\Delta F^\circ_{298} = -70{,}440$ al.

The values recorded by Lewis and Randall for the above reactions are, respectively, 18,280, -78,560 and -69,660. (There is, however, a discrepancy in these values. If the first two are correct, the third apparently should be -69,420.)

The above values for sulphur dioxide are recommended for temporary and immediate use, but may be subject to further correction when the thermodynamics of the reaction $Cu_2S + 2Cu_2O = 4Cu + SO_2$ has been satisfactorily discussed. Work on certain phases of this reaction is now in progress at the Pacific Experiment Station of the U. S. Bureau of Mines.

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